

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
10 May 2002 (10.05.2002)

PCT

(10) International Publication Number
WO 02/36654 A2

- (51) International Patent Classification⁷: C08G 18/06, 18/42 (74) Agent: REITENBACH, Daniel; Crompton Corporation, 199 Benson Road, Middlebury, CT 06749 (US).
- (21) International Application Number: PCT/US01/50532 (81) Designated States (*national*): CA, KR.
- (22) International Filing Date: 19 October 2001 (19.10.2001) (84) Designated States (*regional*): European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR).
- (25) Filing Language: English
- (26) Publication Language: English Published:
— without international search report and to be republished upon receipt of that report
- (30) Priority Data:
09/699,808 30 October 2000 (30.10.2000) US
- (71) Applicant: CROMPTON CORPORATION [US/US]; 199 Benson Road, Middlebury, CT 06749 (US).
For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.
- (72) Inventors: BECHARA, Ibrahim; 80 Orchard Hill Road, Carmel, NY 10512 (US). CHANG, Biau-Hung; 3 Aberdeen Place, Basking Ridge, NJ 07920 (US). ILMENEV, Pavel; 62 Bob Hill Road, Ridgefield, CT 06877 (US).



WO 02/36654 A2

(54) Title: ANIONIC POLYURETHANE DISPERSION

(57) Abstract: An anionic polyurethane dispersion having compatibility with, and adhesivity to non-polar substrates, such as polyolefins, which includes a reaction product of a prepolymer and a chain extender. The prepolymer includes a hydroxylated polymer, a polyisocyanate and a hydroxylated compound having a pendent acid group. In one embodiment the prepolymer is limited by the requirement that the pendent acid group of the hydroxylated compound is a sulfonic acid group. In a second embodiment the prepolymer is limited by the requirement that the reaction product include an ester of a hydroxylated fatty acid having about 12 to about 20 carbon atoms. In a third embodiment the dispersion is limited by the requirement that the prepolymer reaction product include a hydrocarbon segment containing at least about 12 carbon atoms and the chain extender is a hydroxylated amine compound.

WO 02/36654

PCT/US01/50532

ANIONIC POLYURETHANE DISPERSION

BACKGROUND OF THE DISCLOSURE

5

1. Field of the Invention

The present invention is directed to an anionic polyurethane dispersion having high functionality. More specifically, the present invention is drawn to an anionic polyurethane dispersion having excellent adhesion to non-polar substrates.

10

2. Background of the Prior Art

A major problem associated with coating and bonding of polyurethane dispersions to non-polar substrates, of which polyolefins is a major example, is the poor adhesion therebetween. Other problems associated with polyurethane dispersion coatings and adhesives are their poor performance when blended with non-polar materials, such as polyolefin emulsions, and their poor acid and alkaline resistance.

15

The aforementioned problems have been recognized in the art. Those skilled in the art have appreciated that these problems may be addressed by providing chemical moieties in the coating or adhesive common to the matrix or substrate upon which the coating or adhesive is disposed. Thus, attempts have been made to include chemical moieties of the type included in the substrate or matrix in the polyurethane dispersion coating or adhesive.

20

25

An example of this expedient is provided in U.S. Patent 5,672,653. That patent discloses an anionic waterborne dispersion which includes hydroxy-terminated polybutadiene to produce films and adhesives.

30

WO 02/36654

PCT/US01/50532

Other solutions are provided in other U.S. patents. U.S. Patent 4,240,944 describes a binder composition and a method of employing that composition in glass fiber sizing compositions. The binder composition of the '944 patent is an aqueous emulsion containing isotactic carboxylated polypropylene, base
5 and surfactant.

U.S. Patent 4,507,430 sets forth a water-based polyurethane emulsion containing a hydrogenated polyalkadiene polyol component.

10 Finally, U.S. Patent 4,728,573 is drawn to an aqueous treating composition which includes at least one amino coupling agent and an aqueous emulsion of an acid or anhydride-modified polyolefin containing one or more surfactants. The polyolefin is neutralized with an organic or inorganic base having a basicity less than the basicity of the amino moiety of the coupling agent. The aqueous
15 treating composition further comprises a binder stabilizer, one or more film-forming polymers and water.

Although these disclosures have advanced the state of the art, still there is a pressing need for a coating and adhesive polyurethane dispersion composition that
20 better bonds to polyolefin and other non-polar substrates, better blends with polyolefin and other non-polar species and provides good acid and alkaline resistance.

BRIEF SUMMARY OF THE INVENTION

25 A new anionic polyurethane dispersion has now been developed which provides enhanced functionality so that improved compatibility and adhesivity of polyurethane dispersions to non-polar substrates, such as polyolefins, is provided.

In accordance with the present invention an anionic polyurethane
30 dispersion is provided. In one preferred embodiment the dispersion is a reaction

WO 02/36654

PCT/US01/50532

product of a prepolymer and a chain extender. The prepolymer is a reaction product of a hydroxylated polymer selected from the group consisting of polyether polyols, polyester polyols and mixtures thereof, a polyisocyanate, and a hydroxylated compound having a pendent sulfonic acid group.

5

In further accordance with the present invention a second preferred embodiment of the anionic polyurethane dispersion of the present invention is again provided by a reaction product of a prepolymer and a chain extender. The prepolymer is a reaction product of a hydroxylated polymer selected from polyols the group consisting of polyether polyols, polyester polyols, and mixtures thereof, a polyisocyanate, a hydroxylated compound having a pendent carboxylic acid group and an ester of a fatty acid having about 12 to about 20 carbon atoms which contains hydroxyl groups.

15

In yet further accordance with the present invention a third preferred embodiment of the anionic polyurethane dispersion is provided. In this embodiment the dispersion is a reaction product of a prepolymer and a hydroxylated amine chain extender. The prepolymer is a reaction product of a hydroxylated polymer selected from the group consisting of a polyether polyol, a polyester polyol and mixtures thereof, a hydroxylated compound containing a hydrocarbon group of at least about 15 carbon atoms, a polyisocyanate and a hydroxylated compound having a pendent acid group.

20

DETAILED DESCRIPTION

25

The anionic polyurethane dispersion having enhanced functionality of the present invention is a reaction product of a prepolymer and a chain extender. In all embodiments the first component of the prepolymer is a hydroxylated polymer which may be a polyether polyol, a polyester polyol or mixtures thereof. In the preferred embodiment wherein the hydroxylated polymer is a polyether polyol, it is

30

WO 02/36654

PCT/US01/50532

preferred that the polyether polyol be a polyalkylene glycol. The polyalkylene glycol is preferably polyethylene glycol, polypropylene glycol or mixtures thereof.

In the alternate preferred embodiment wherein the hydroxylated
5 polymer is a polyester polyol, it is preferred that the polyester polyol be a polyester glycol. Among preferred polyester glycols are poly(hexamethylene adipate/isophthalate) glycol and poly(hexamethylene orthophthalate)glycol.

A second component, common to all embodiments of the present
10 invention, that reacts to form the reaction product of the prepolymer, is a polyisocyanate. Although any compound possessing at least two isocyanate groups is within the contemplation of the present invention, it is preferred that the polyisocyanate be a diisocyanate.

Both aliphatic and aromatic polyisocyanates may be utilized in the
15 formation of the prepolymer. However, aliphatic polyisocyanates are preferred. Thus, such aliphatic diisocyanates as isophorone diisocyanate (IPDI), hexamethylene diisocyanate, dicyclohexylmethane-4,4-diisocyanate and the like are preferred for inclusion in the prepolymer reaction product.

20

In the first preferred embodiment of the prepolymer of the
polyurethane dispersion the third component of the prepolymer reaction product is a hydroxylated compound containing a pendent sulfonic acid group.

25 Although the prepolymer of the first embodiment of the present invention may be limited to the aforementioned three components, one or more additional components, which generically can be defined as a hydroxylated compound containing a hydrocarbon segment having at least about 12 carbon atoms, can also be provided.

30

WO 02/36654

PCT/US01/50532

One preferred class of hydroxylated compounds containing a hydrocarbon segment is a hydroxylated polyalkadiene. The hydroxylated polyalkadiene may or may not be hydrogenated. If hydrogenated, the degree of hydrogenation may be partial or complete. A preferred class of hydroxylated polyalkadienes is the class of polyalkadiene diols. A particularly preferred class of hydroxylated polyalkadienes are hydroxylated polybutadienes.

Another class of preferred hydroxylated compounds containing a hydrocarbon segment is a class of esters of a fatty acid having about 12 to about 20 carbon atoms containing hydroxyl groups. More preferably, this class of esters of fatty acids having about 15 to about 20 carbon atoms and contains hydroxyl groups. Still more preferably, an ester is a fatty acid having about 18 carbon atoms containing hydroxyl groups is utilized. Thus, a particularly preferred ester for use in the prepolymer reaction product is glycerol monostearate (GMS).

15

The chain extender, which reacts with the prepolymer to form the polyurethane dispersion, is preferably an amine compound. More preferably, a diamine, whether aliphatic or aromatic, is utilized. Of the diamines, the simplest and one that is particularly preferred is hydrazine.

20

In a second preferred embodiment of the prepolymer of the anionic polyurethane dispersion of the present invention, the prepolymer reaction product includes the aforementioned hydroxylated polymer polyisocyanate components, as defined in the discussion of the first embodiment. In this second embodiment, however, the employment of a hydroxylated compound containing a hydrocarbon segment is not optional. Rather, it is essential. Specifically, in this embodiment an ester of a hydroxylated fatty acid containing about 12 to about 20 carbon atoms is required. The preferred and more preferred embodiments of this class of compounds discussed above, are applicable. As discussed above, in the discussion of the first

WO 02/36654

PCT/US01/50532

embodiment, glycerol monostearate is a particularly preferred component of the prepolymer reaction product of this second embodiment.

Although the above remarks, emphasizing the criticality of an ester of
5 a fatty acid containing hydroxyl groups narrows the scope of the prepolymer of the second embodiment compared to the first embodiment, the second embodiment is broader than the first embodiment insofar as a requirement of the first embodiment, that the prepolymer include a hydroxylated compound containing a pendent sulfonic acid group, is, in the second embodiment, extended to any hydroxylated compound
10 containing a pendent acid group. As such, this component may be a hydroxylated compound containing a pendent sulfonic acid group as well a hydroxylated compound containing a pendent carboxylic acid group. For example, dimethylol propionic acid (DMPA), an example of the latter class of compounds, is particularly preferred.

15 In the third preferred embodiment of the anionic polyurethane dispersion of the present invention, the prepolymer is a reaction product of a hydroxylated polymer, a polyisocyanate, a hydroxylated compound containing a pendent acid group and a hydroxylated compound including a hydrocarbon segment containing at least about 12 carbon atoms. It is emphasized that the latter component
20 may be a hydroxylated polyalkadiene, an ester of a fatty acid or both.

What distinguishes the third preferred embodiment of polyurethane dispersions of the present invention from the first two embodiments is the identity of the chain extender. In this third preferred, embodiment, the chain extender is limited
25 to functionalized amine compounds. As in the first and second embodiments a diamine, albeit functionalized, is preferred. Preferred functionalized amines include hydroxylated amines, such as aminoethylaminoethanol, and unsaturated amines, such as diethylene triamine.

WO 02/36654

PCT/US01/50532

The following examples are given to illustrate the present invention. Since these examples are given for illustrative purposes only, the invention should not be deemed limited thereto.

WO 02/36654

PCT/US01/50532

EXAMPLE 1Preparation of High FunctionalityAnionic Polyurethane Dispersion

5

Poly(hexamethylene adipate/isophthalate) glycol having an average molecular weight of 3030 (121.27 g) (Fomrez ® 8066-37, a product of Crompton Corp.), a hydroxylated polybutadiene having an average molecular weight of 2,400 (121.27 g) (Poly bd ® R45HTLO, a product of Elf Atochem), isophorone diisocyanate (122.42 g) (IPDI), dimethylol propionic acid (35.05 g) (DMPA) and 1-methyl-2-pyrrolidinone (100.0 g) (M-Pyrol) were charged into a reaction flask and reacted at 90°C until the NCO concentration reached the calculated value of 3.4% (about 3 hours). The thus formed prepolymer was thereupon dispersed in water (648.46 g) to which triethylamine (29.18 g) (TEA) and a defoamer (0.8 g) was added.

15 The completely dispersed prepolymer was extended employing the hydroxylated amine, aminoethylaminoethanol (18.78 g).

The resultant stable dispersion product had a solids content of 34.4%, a pH of 8.7 and viscosity of 140 cps (Brookfield 7 LV, spindle #3 at 60 rpm). This

20 dispersion is summarized in Table 1.

WO 02/36654

PCT/US01/50532

COMPARATIVE EXAMPLE 1Preparation of Anionic Polyurethane Dispersion

5 Example 1 was substantially identically reproduced. However, the aminoethylaminoethanol chain extender of that example was replaced with a 35% solution of aqueous hydrazine (16.45 g).

 A summary of Comparative Example 1, including the results of this
10 example, is provided in Table 1.

WO 02/36654

PCT/US01/50532

TABLE 1

Prepolymer Constituents, g							Polyurethane Dispersion		
Example No.	Fomrez ® 8066-37	Poly bd ® R45HTLO	IPDI	DMPA	M-Prol	Chain Extender, g	Solids Content, %	pH	Visc, cps
1	121.27	121.27	122.42	35.05	100.00	Aminoethylaminoethano 1, 18.78	34.4	8.7	140
CE1	121.43	121.43	122.16	34.98	100.00	35% Aqueous Hydrazine Soln, 16.75	35.8	8.6	180

WO 02/36654

PCT/US01/50532

EXAMPLE 2Preparation of Films of the Polyurethane Dispersion

5 The polyurethane dispersions of Example 1 and Comparative Example 1 were cast on glass plates. The dispersions disposed on glass plates were dried to form films having thicknesses of about 5 mils. The thus formed films were removed from the glass plates upon which they were cast and cut into samples using a standard die-cut knife.

10

 These films were tested, on an Instron ® Model 4500, at a 20 in/min jaw separation rate to obtain the ultimate tensile strength and elongation at break properties of the films.

15

 A summary of this example appears in Table 2.

WO 02/36654

PCT/US01/50532

EXAMPLE 3Preparation of Melamine-Formaldehyde Containing Polyurethane Dispersion Films

5 The polyurethane dispersions of Example 1 and Comparative Example
1 were combined with melamine formaldehyde resin such that the melamine
formaldehyde resin was present in a concentration of 5% by weight, based on the
weight of the polyurethane dispersion. The thus formed compositions were formed
into films in accordance with the procedure of Example 2. The films were tested in
10 accordance with the procedure of Example 2.

Example 3 is summarized in Table 2.

WO 02/36654

PCT/US01/50532

TABLE 2

Film of Example No.	% Melamine Formaldehyde	Ultimate Tensile Strength, psi	Elongation at Break, %
1	0	4,100	390
CE 1	0	3,500	390
1	5	5,450	170
CE 1	5	5,150	200

WO 02/36654

PCT/US01/50532

Discussion of Table 2

The results summarized in Table 2 establish that the anionic polyurethane dispersion of the present invention provides greater tensile strength, at
5 identical elongation, compared to polyurethane dispersions of the prior art. In addition, the inclusion of 5% melamine formaldehyde, which acts as a curing agent, further increases the tensile strength of polyurethane dispersions within the scope of the present invention and those of the prior art.

10 These examples emphasize the beneficial effect of higher crosslinkage density of the dispersion of the present invention compared to the dispersions of the prior art. As those skilled in the art are aware, higher crosslink density increases the toughness, hardness and chemical resistance of polyurethane films. This higher
crosslink density results from the higher number of crosslinkable functional groups
15 provided in the present invention over the reactants forming the polyurethane dispersions of the prior art.

WO 02/36654

PCT/US01/50532

EXAMPLE 4Preparation of a Polyurethane Dispersion

5 Formez ® 8066-37 (344.11 g); glycerol monostearate (38.14 g)
(GMS); DMPA (10.01 g); and IPDA (104.21 g) were charged into a reaction flask
equipped with a stirrer. The thus charged reactants were heated at 90° C until the
NCO concentration of the product reached the calculated value of 4.72% (about 3
hours). The resultant prepolymer was dispersed in water (331.47 g) to which a
10 nonionic surfactant (44.79 g) (Igepal ® CO-730, produced by Rhodia), triethylamine
(8.34 g) TEA and a defoamer (0.8 g) was added. The resultant, completely dispersed
prepolymer was chain extended by adding a 35% aqueous hydrazine solution (9.0 g).

 The final product was a stable, viscous dispersion having a solids
15 content of 61.9% and a pH of 7.7.

A summary of this dispersion appears in Table 3.

WO 02/36654

PCT/US01/50532

COMPARATIVE EXAMPLE 2Preparation of a Polyurethane Dispersion

- 5 A polyurethane dispersion substantially identical to the polyurethane dispersion of Example 4 but for the omission of GMS was prepared in accordance with the procedure of Example 4.

A summary of this example is included in Table 3.

WO 02/36654

PCT/US01/50532

TABLE 3

Prepolymer Components, g					Chain Extender, g	Dispersion Properties	
Polyurethane Dispersion of Example No.	Formez ® 8066-37	GMS	DMPA	IPDA	35% Aq Hydrazine Soln	Solids Content, %	pH
4	344.11	38.14	10.01	104.2 1	9.00	61.9	7.7
CE 2	432.60	0	3.90	60.00	8.04	62.0	7.8

WO 02/36654

PCT/US01/50532

EXAMPLE 5Peel Adhesion Test

5 The polyurethane dispersions of Example 4 and Comparative Example
2 were separately blended with a carboxylated wax in a weight ratio of polyurethane
dispersion to carboxylated wax of 1:1. The resultant composition was cast upon an
untreated polypropylene sheet (30 mils thick) and dried at room temperature.
Following drying, the resultant cast sheet was annealed by subjecting it to a
10 temperature of 248° F for 15 minutes. The cast sheet was thereupon laminated to
another 30 mil thick polypropylene sheet under a pressure of 60 psi at 300° F for 30
seconds.

 The laminates were subjected to a peel adhesion test in accordance
15 with ASTM Test Procedure D 1876. The results of this test are summarized in Table
4.

WO 02/36654

PCT/US01/50532

TABLE 4

Laminate Using PUD of Exam No.	Peel Adhesion, pounds/linear in.
4	1.5
CE 2	No adhesion

WO 02/36654

PCT/US01/50532

DISCUSSION OF RESULTS OF TABLE 4

The inclusion of glycerol monostearate improves the adhesivity of a blend of wax and the anionic polyurethane dispersion of Example 4 to the non-polar substrate polypropylene, as manifested by the peel adhesion test relative to the prior art anionic polyurethane dispersion of Comparative Example 2 in which it is omitted. This is so insofar as the sole distinction between the polyurethane dispersion of Example 4 and the polyurethane dispersion of Comparative Example 2 is the presence of glycerol monostearate. Indeed, the absence of glycerol monostearate, as illustrated by the results summarized in Table 4, is essential to effective adhesive properties.

WO 02/36654

PCT/US01/50532

EXAMPLE 6Preparation of an Anionic Polyurethane Dispersion

5 N,N-bis-(2-hydroxyethyl)-2-aminoethane-sulfonic acid (20.20 g)
(BES) was introduced into a 1-liter glass reactor equipped with a stirrer and a heater.
1-Methyl-2-pyrrolidinone (60.0 g) (M-Pyrol) in the presence of TEA (10.64 g) was
next introduced into the temperature controlled reactor. This was followed by the
introduction of polypropylene glycol diol having a molecular weight of 2000 (69.45
10 g) (Poly-G ® 20-56, a product of Arch Chemicals), hydroxylated polybutadiene
having an average molecular weight of 2400 (69.45 g) (Poly bd ® R45HTLO, a
product of Elf Atochem) and IPDI (45.76 g). The reactor was then heated at 80°C for
about 3 hours at which time the resultant prepolymer reached the NCO calculated
value of 4.43%. The prepolymer was dispersed in water (355.32 g) containing
15 defoamer (0.8 g). After the polymer was completely dispersed, the prepolymer was
extended with a 35% aqueous solution of hydrazine (11.58 g).

The product, an anionic polyurethane dispersion was stable having a
38.1% solids content, a pH of 6.5 and a viscosity of 500 cps (Brookfield ® LV,
20 spindle #3 at 60 rpm).

A summary of this example appears in Table 5.

WO 02/36654

PCT/US01/50532

COMPARATIVE EXAMPLE 3Preparation of Anionic Polyurethane

5 Example 6 was substantially reproduced but for the substitution of DMPA for BES as the stabilizer.

A summary of this comparative example is included in Table 5.

WO 02/36654

PCT/US01/50532

COMPARATIVE EXAMPLE 4Preparation of an Anionic Polyurethane Dispersion

5 An anionic polyurethane dispersion was prepared in accordance with
the procedure employed in the formation of the polyurethane dispersion of Example 6
but for two distinctions. The first was the substitution of the hydroxylated polyester
Fomrez ® 8066-37, within the scope of the present invention, for the polypropylene
glycol diol, Poly-G ® 20-56. The second distinction was the absence of the
10 hydroxylated polybutadiene, Poly bd ® R45HTOL.

A summary of Comparative Example 4 is included in Table 5.

WO 02/36654

PCT/US01/50532

TABLE 5

Polyurethane Dispersion of Example No.	Prepolymer, g					Dispersant, g				Chain Extender, g	Polyurethane Dispersion		
	Hydroxylated Polymer, g	Poly db ® 45HTLO	IPDI	Stabilizer	M-Pyrol	Water	TEA	Defoamer	% Solids Content		pH	Visc, cps	
CE3	Poly G 20-56, 138.80	52.93	62.69	DMPA, 10.59	15.0	505.11	8.81	0.8	7.50		34.5	7.9	1200
6	Poly G 20-56, 69.45	69.45	70.27	BES, 20.20	60.0	355.32	10.64	0.8	11.58		38.1	6.5	500
CE4	Fomrez 7 8066-37, 178.95	None	45.76	BES, 15.29	60.0	377.67	8.05	0.8	5.41		32.0	6.5	60

WO 02/36654

PCT/US01/50532

EXAMPLE 7Peel Adhesion of Polyurethane DispersionsBlended with a Wax Emulsion

5

Compositions comprising equal weight mixtures of an aqueous emulsion of carboxylated polypropylene wax and the polyurethane dispersions of Examples 4 and 6 and Comparative Examples 1 to 4 were prepared. These compositions, as well as neat carboxylated polypropylene wax, were sandwiched
10 between polypropylene sheets in accordance with the procedure of Example 5.

The peel adhesivity, in pounds per linear inch (pli), of each of the tested compositions as well as their mode of failure is included in Table 6.

WO 02/36654

PCT/US01/50532

TABLE 6

Adhesive	Peel Adhesion, pli	Mode of Failure
Emulsion of Carboxylated Polypropylene Wax (CPW)	0	Not Applicable
Blend of PUD of CPW CE 1 +	1.35	Cohesive
Blend of PUD of CPW Ex. 4 +	1.53	Cohesive
Blend of PUD of CPW CE2 +	0.80	Adhesive
Blend of PUD of CPW CE4 +	1.51	Adhesive
Blend of PUD of CPW Ex6 +	1.50	Cohesive
Blend of PUD of CPW CE3 +	1.34	Cohesive

WO 02/36654

PCT/US01/50532

Discussion of Results of Table 6

The results summarized in Table 6 establish the improved results obtained by the polyurethane dispersions within the scope of the present invention. The comparison between the polyurethane dispersions of Example 4 and Comparative Example 2 establishes the criticality of the inclusion of a long chain hydrocarbon group provided by glycerol monostearate in providing adhesivity of the dispersion when applied to polypropylene. This is manifested by the markedly improved adhesivity of the polyurethane dispersion of Example 4 over the polyurethane dispersion of Comparative Example 2. It is emphasized that the major distinction between these anionic polyurethane dispersions is the inclusion and exclusion, respectively, of that component in the former and latter of those two polyurethane dispersions. It is also noted that the mode of failure of the dispersions of both of these examples is the breakup of the polyurethane polymer rather than the breakup of the bond of the polyurethane polymer to the polypropylene substrate.

The comparison between the polyurethane dispersions of Example 6 and Comparative Example 3 illustrates the improved result obtained by utilizing a hydroxylated compound with a pendent sulfonic acid group, compared to a hydroxylated compound with a pendent carboxylic acid group, as a stabilizer in providing unexpectedly improved adhesion. Thus, the unexpected improved peel strength of the PUD of Example 6 over that of Comparative Example 3 is solely due to the only distinction between the two PUD's, the employment of BES, a compound with a pendent sulfonic acid group, in the PUD of Example 6, compared to the inclusion of DMPA, a compound with a pendent carboxylic acid group, in the PUD of Comparative Example 3.

The unexpected result, in comparing the polyurethane dispersions of Example 6 and Comparative Example 4, is the failure mode. The polyurethane dispersion of Comparative Example 4 failed adhesively whereas the polyurethane

WO 02/36654

PCT/US01/50532

dispersion of Example 6 failed cohesively. A cohesive failure indicates that adhesion of the polyurethane wax blend to the polypropylene substrate exceeds the strength of the polymer itself. This demonstrates that the polypropylene dispersion of Example 6 provides higher adhesion than does the polyurethane dispersion of Comparative Example 4.

The above embodiments and examples are provided to illustrate the scope and spirit of the present invention. These embodiments and examples will make apparent, to those skilled in the art, other embodiments and examples. These other embodiments and examples are within the scope of the present invention. Therefore, the present invention should be limited only by the appended claims.

WO 02/36654

PCT/US01/50532

WHAT IS CLAIMED IS:

- 1 1. An anionic polyurethane dispersion comprising a reaction product
2 of a prepolymer and a chain extender, said prepolymer being a reaction product of a
3 hydroxylated polymer selected from the group consisting of a polyether polyol, a
4 polyester polyol, or a mixture thereof, a polyisocyanate and a hydroxylated compound
5 having a pendent sulfonic acid group.
- 1 2. A dispersion in accordance with Claim 1 wherein said prepolymer
2 includes a hydroxylated polyalkadiene.
- 1 3. A dispersion in accordance with Claim 2 wherein said hydroxylated
2 polyalkadiene is partially or totally hydrogenated.
- 1 4. A dispersion in accordance with Claim 1 wherein said prepolymer
2 includes an ester of a hydroxylated fatty ester containing about 12 to about 20 carbon
3 atoms.
- 1 5. A dispersion in accordance with Claim 1 wherein said chain
2 extender is an amine compound.
- 1 6. A dispersion in accordance with Claim 1 wherein said hydroxylated
2 compound having a pendent sulfonic acid group is N,N-bis(2-hydroxyethyl)-2-
3 aminoethanesulfonic acid.
- 1 7. An anionic polyurethane dispersion comprising a reaction product
2 of a prepolymer and a chain extender, said prepolymer being a reaction product of a
3 hydroxylated polymer selected from the group consisting of a polyether polyol, a
4 polyester polyol or a mixture thereof, a polyisocyanate, a hydroxylated compound
5 having a hydrocarbon segment containing at least about 12 carbon atoms and a

WO 02/36654

PCT/US01/50532

6 hydroxylated compound having a pendent acid group, said chain extender being a
7 hydroxylated amine compound.

1 8. A dispersion in accordance with Claim 7 wherein said hydroxylated
2 compound having a hydrocarbon segment is a hydroxylated polyalkadiene.

1 9. A dispersion in accordance with Claim 8 wherein said hydroxylated
2 polyalkadiene is partially or totally hydrogenated.

1 10. A dispersion in accordance with Claim 7 wherein said prepolymer
2 hydroxylated compound having a hydrocarbon segment is an ester of a hydroxylated
3 fatty acid containing between about 12 to about 20 carbon atoms.

1 11. A dispersion in accordance with Claim 7 wherein said
2 functionalized amine chain extender is selected from the group consisting of
3 hydroxylated amines and unsaturated amines.

1 12. A dispersion in accordance with Claim 11 wherein said
2 functionalized amine chain extender is aminoethylaminoethanol.

1 13. A dispersion in accordance with Claim 11 wherein said
2 functionalized amine chain extender is diethylene triamine.

1 14. An anionic polyurethane dispersion comprising a reaction product
2 of a prepolymer and a chain extender, said prepolymer being a reaction product of a
3 hydroxylated polymer selected from the group consisting of a polyether polyol, a
4 polyester polyol and mixtures thereof, an ester of a hydroxylated fatty acid having
5 between about 12 and about 20 carbon atoms, a polyisocyanate and a hydroxylated
6 compound having a pendent acid group.

WO 02/36654

PCT/US01/50532

1 15. A dispersion in accordance with Claim 14 wherein said ester of a
2 hydroxylated fatty acid has between about 15 and about 20 carbon atoms.

1 16. A dispersion in accordance with Claim 15 wherein said ester of a
2 hydroxylated fatty acid has about 18 carbon atoms.

1 17. A dispersion in accordance with Claim 16 wherein said ester of a
2 hydroxylated fatty acid is a stearate.